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CITATION:

Xu, Fei ...[et al]. The first crystallographic example of a face-sharing fluoroaluminate anion Al_(2)F_(9)^(3-).. Dalton transactions 2013, 42(6): 1965-1968

ISSUE DATE:

2013-02-14

URL:

http://hdl.handle.net/2433/182044

The first crystallographic example of a face-sharing fluoroaluminate anion $Al_2F_9^{3-}$

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

Abstract

The first example of a face-sharing fluoroaluminate anion, $Al_2F_9^{3-}$, is crystallographically determined in $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754}$ ($C_{18}MIm^+$ = 1-methyl-3-octadecylimidazolium cation), and the geometry and bond properties therein are discussed with the aid of quantum chemical calculations.

The structural diversity of aluminium fluoride and fluoroaluminate anions has attracted considerable research interest,[1–3] partly because of the interest in aluminium fluoride as a Lewis acidic catalyst.[4–6] A large number of fluoroaluminate anions have been crystallographically determined by introducing metal or organic cations. Although the tetrahedral AlF_4^- anion was determined in three salts with large organic cations,[7,8] most fluoroaluminate anions consist of an octahedral AlF_6 unit.[9–14] The trigonal bipyramidal AlF_5^{2-} anion has not been determined crystallographically, but was spectroscopically observed in a tetramethylammonium salt.[15] The simplest form of fluoroaluminate anion based on the octahedral AlF_6 unit is AlF_6^{3-} and larger isolated species.[16–26] In a few rare cases, edge-sharing bioctahedral motifs were observed in dinuclear,[8,27,28] chain-like[7,29,30] and layered[31,32] structures. One of the cases missing from this series is the face-sharing structure of the bioctahedral $Al_2F_9^{3-}$ anion. Although such a structure was predicted in molten salts,[33] no crystallographic work has been reported until now. The small ionic radii of the F and Al atoms, *i.e.* the short Al–F bond, lead to difficulty in forming this type of crowded ion. In this communication, the geometry and bond properties of the first face-sharing fluoroaluminate anion, $Al_2F_9^{3-}$, are discussed in comparison with known fluoroaluminate species.

The starting compound, $[C_{18}MIm][AlF_4]$, was prepared by the reaction of $[C_{18}MIm][AlCl_4]$ and a large excess of anhydrous HF followed by elimination of the residual HF and byproduct HCl under vacuum. The $Al_2F_9^{3-}$ anion was determined in $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_n$, which was obtained during an attempt to grow single crystals of $[C_{18}MIm][AlF_4]$ (1-methyl-3-octadecylimidazolium tetrafluoroaluminate) by slow evaporation of the solvent from a CH_2Cl_2 solution.‡ Two CH_2Cl_2 molecules are found in the asymmetric unit, but their site occupancies are lower than 1 (0.944 and 0.810), resulting in n = 1.754. The site occupancies of CH_2Cl_2 seem to depend on the evacuation time, and the powder X-ray diffraction pattern of the sample after it was thoroughly pumped at room temperature was completely different from the simulated pattern from the single crystal structure of $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754}$. The reaction that occurred during the crystallisation is

most probably written as:

$$3[C_{18}MIm][AlF_4] + nCH_2Cl_2 \rightarrow [C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_n + AlF_3$$

The formation of $Al_2F_9^-$ and loss of AlF_3 probably result from the large stabilization energy by forming a lattice including CH_2Cl_2 molecules. Crystalline $[C_{18}MIm][Al_2F_9](CH_2Cl_2)_n$ with insoluble white powder (probably AlF_3) was reproducibly obtained although the quality of the crystals was not always suitable to fully complete single-crystal X-ray diffraction analysis. The $Al_2F_9^{3-}$ anion consists of two face-sharing AlF_6 octahedra and has a roughly D_{3h} symmetry as shown in Fig. 1. The six bridging Al–F_b bonds (1.874(2)–1.959(3) Å) and the six terminal Al–F_t bonds (1.723(2)–1.750(2) Å) in $Al_2F_9^{3-}$ are longer and shorter, respectively, than the Al–F bond in the octahedral AlF_6^{3-} (*ca.* 1.80 Å),[10–14] where F_b and F_t denote the bridging and terminal F atoms in $Al_2F_9^{3-}$, respectively. Accordingly, the F_t–Al–F_t angles (94.24(12)°–99.81(13)°) are larger than the F_b–Al–F_b angles (74.47(10)°–77.81(10)°) and the two octahedra in $Al_2F_9^{3-}$ are slightly distorted from the ideal O_h symmetry. Bond valence sums of the two Al atoms in $Al_2F_9^{3-}$ are 2.91 and 2.95 according to the literature.[34,35] These values are consistent with the oxidation state of +3 for Al as in the cases of the isolated AlF_4^- (2.98 and 3.02)[7] and AlF_6^{3-} (2.96)[13] anions (see

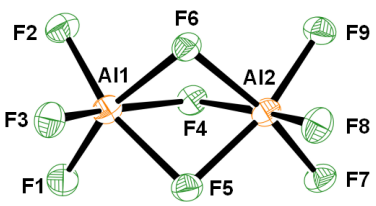

Fig. 1 The structure of $Al_2F_9^{3-}$ with atom numbering scheme. Selected bond lengths (Å) and angles (°): Al–F_t range, 1.723(2)–1.750(2); Al–F_b range, 1.874(2)–1.959(3); F_t–Al–F_t range, 94.24(12)–99.81(13); F_b–Al–F_b range, 74.47(10)–77.81(10), where F_t and F_b denote terminal (F1, F2, F3, F7, F8 or F9) and bridging F atoms (F4, F5 or F6). See Table S2, ESI† for the detailed values.

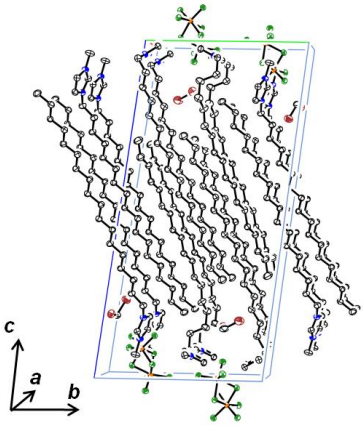

Fig. 2 Unit cell of $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754}$ at –100 °C.

Table S4, ESI† for the calculation of bond valence sums).

Such a face-sharing $M_2F_9^{3-}$ structure (M denotes the metal atom) was observed only in three examples with transition metals ($Cr_2F_9^{3-}$, $V_2F_9^{3-}$ and $Fe_2F_9^{3-}$) when organic ammonium cations ($(CH_3)_4N^+$ [36] and $(C_2H_5)_4N^+$)[37] were introduced. Although their geometries are similar, the M–F_t and M–F_b bond lengths in $Al_2F_9^{3-}$ are significantly shorter than those in the transition metal species (1.987, 2.033 and 2.024 Å for Cr–F_b, V–F_b and Fe–F_b; 1.838, 1.852 and 1.861 Å for Cr–F_t, V–F_t and Fe–F_t, respectively). Consequently, the M···M distance of $Al_2F_9^{3-}$ (2.6866(19) Å) is shorter than those of $Cr_2F_9^{3-}$ (2.773 Å), $V_2F_9^{3-}$ (2.852 Å) and $Fe_2F_9^{3-}$ (2.907 Å).

The packing mode of $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754}$ is described as the layered structure of domains with high and low polarities (Fig. 2), although this structure is not highly ordered compared to previously known alkylimidazolium salts with long alkyl chains, such as $[C_{18}MIm][AF_6]$ (A = P, As, Sb, Nb, or Ta),[38] $[C_{12}MIm][PF_6]$[39] and $[C_{14}MIm][PF_6]$.[40] The highly polar domains, consisting of $Al_2F_9^{3-}$ anions and imidazolium headgroups, are separated by the low polar domains consisting of interdigitated alkyl chains tilted relative to the polar domain. There are three crystallographically independent cations in the unit cell; the alkyl chain of one cation shows

an all-*trans* conformation (Cation 1, Fig. S1(c), ESI†) and those of the other two cations show bent conformations (Cation 2, bent at C36, Fig. S1(d); Cation 3, bent from C66 to C68, Fig. S1(e), ESI†). The formation of $Al_2F_9^{3-}$ anion may be attributed to the phase separation caused by the amphiphilic cation, $C_{18}MIm^+$, which prevents the anions from coming close to each other to form chain-like structures. The two crystallographically independent CH_2Cl_2 molecules are located near the polar region to fill the space between the alkyl chains.

All the F atoms in the anion are involved in short contacts (below the sum of van der Waals radii, Table S3, ESI†) with H atoms of the imidazolium rings (F2, F3, F4, F5, F7, F8 and F9), alkyl chains (F1, F2, F4, F6, F8 and F9) or CH_2Cl_2 molecules (F3, F8 and F9). Bifurcation of the C–H···F bonds is observed for H atoms which interact with two F atoms (H2 with F4 and F9, H24a with F2 and F4, H32 with F8 and F9, H34 with F3 and F5, H62 with F4 and F7 and H91b with F8 and F9).

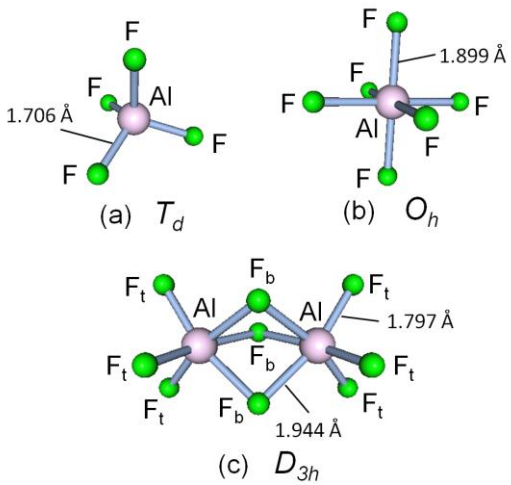

Fig. 3 Calculated geometries of (a) AlF_4^-, (b) AlF_6^{3-} and (c) $Al_2F_9^{3-}$ at MP2/aug-cc-pVTZ. The F_t–Al–F_t and F_b–Al–F_b angles in $Al_2F_9^{3-}$ are 75.1° and 96.2°, respectively.

The calculated geometries of AlF_4^-, AlF_6^{3-} and $Al_2F_9^{3-}$ at MP2/aug-cc-pVTZ are shown in Fig. 3 (see Table S5, ESI† for detailed geometrical parameters and vibrational frequencies calculated

at the MP2, B3LYP and PBE1PBE levels combined with cc-pVTZ and aug-cc-pVTZ basis sets). The calculated Al−F bond lengths in these species were slightly overestimated at all levels of theory compared to the experimental data. The $F_b\cdots F_b$ distance in $Al_2F_9^{3-}$ (2.368 Å) is significantly shorter than the F···F distance in AlF_4^- (2.786 Å) and the *cis*-F···F distance in AlF_6^{3-} (2.686 Å), which is indicative of the steric crowding at the triply bridged part of $Al_2F_9^{3-}$. Natural bond orbital (NBO) charges, valencies and bond orders of the three species are listed in Table 1.[41,42] In all the cases, the difference between the formal charges (+3 for Al and −1 for F) and NBO charges suggests the polar covalent nature of these Al−F bonds. Although the Al atoms in $Al_2F_9^{3-}$ and AlF_6^{3-} have similar positive charges (2.024 for $Al_2F_9^{3-}$ and 2.049 for AlF_6^{3-}), the F atoms in $Al_2F_9^{3-}$ are less negatively charged (−0.808 for F_t and −0.734 for F_b) than that in AlF_6^{3-} (−0.842). The smaller NBO charge of F_t in $Al_2F_9^{3-}$ relative to that in AlF_6^{3-} is caused by the shorter Al−F bond, whereas the NBO charge of F_b is determined by the balance of two factors: the longer $Al-F_b$ bond and the sharing of F_b between the two Al atoms. By forming the $Al_2F_9^{3-}$ bioctahedral structure, the Al−F bond order decreases from 0.376 to 0.286 for $Al-F_b$ and increases from 0.376 to 0.415 for $Al-F_t$, which indicates that the $Al-F_b$ and $Al-F_t$ bonds become more and less polar, respectively. These changes in bond order reflect the changes in bond length. Consequently, the valency (the sum of bond orders) of the Al atom in $Al_2F_9^{3-}$ (2.104) is smaller than that in AlF_6^{3-} (2.257). The Al−F bond in the tetrahedral AlF_4^- exhibits the largest bond order of 0.498 among the three species, which results from the short Al−F bond in this sterically less crowded species.

In summary, the first face-sharing fluoroaluminate anion, $Al_2F_9^{3-}$, was crystallographically determined in $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754}$. It consists of two face-sharing AlF_6 octahedra and has a roughly D_{3h} symmetry. The two AlF_6 units in $Al_2F_9^{3-}$ are distorted from the ideal octahedral geometry and corresponding changes in bond order were observed.

Table 1 Natural bond orbital charges, valencies and bond orders for AlF_4^-, AlF_6^{3-} and $Al_2F_9^{3-}$ at MP2/aug-cc-pVTZ (see Fig. 3 for the naming of the atoms and Table S5, ESI† for the other results).

	Charges [Valencies][a]	Bond orders[b]
	AlF_4^- (T_d)	
Al	2.108 [1.992]	
F	−0.777 [0.498]	
Al−F		0.498
	AlF_6^{3-} (O_h)	
Al	2.049 [2.257]	
F	−0.842 [0.376]	
Al−F		0.376
	$Al_2F_9^{3-}$ (D_{3h})	
Al	2.024 [2.104]	
F_t	−0.808 [0.415]	
F_b	−0.734 [0.572]	
$Al-F_t$		0.415
$Al-F_b$		0.286

[a] Only the Al−F bonds were considered in calculation of valencies and other minor contributions are ignored here. [b] Atom-atom overlap-weighted natural atomic orbital bond orders.

Notes and references

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†Electronic Supplementary Information (ESI) available: Additional experimental details, computational and crystallographic data. CCDC 906618. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

‡Experimental details are described in ESI†. Crystal data for $[C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754}$: $C_{67.75}H_{132.51}N_6F_9Al_2Cl_{3.51}$, M = 1380.67, triclinic, space group P–1 (no. 2), a = 8.8125(6) Å, b = 14.8052(10) Å, c = 30.847(2) Å, α = 96.083(2)°, β = 99.426(2)°, γ = 90.012(2)°, V = 3947.3(5) Å^3, Z = 2. T = 173 K, D_c = 1.162 g cm^{-3}, $F(000)$ = 1495, R_1 = 0.0702 (810 parameters), wR_2 = 0.1752 [$I > 2\sigma(I)$], GOF = 1.054 for all 12675 data. CCDC 906618.

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